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## ENERGY & ENVIRONMENT DIVISION

CATALYTIC LIQUEFACTION OF BIOMASS

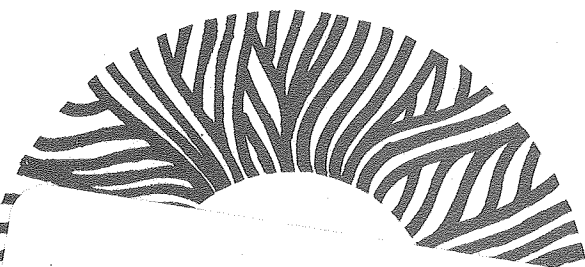
Manu Seth, Roger Djafar, Gary Yu, and Sabri Ergun

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CATALYTIC LIQUEFACTION OF BIOMASS

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### ABSTRACT

The subproject is divided into five tasks which cover exploratory research, investigation of process variables, investigation of process improvement options, product characterization, and product upgrading. In the first task, two new concepts for biomass liquefaction are being explored. The first involves solvolytic depolymerization of wood followed by hydrogenation of the resulting slurry (or solution). During this quarter we have studied the effectiveness of various wood-derived solvents for the solvolytic degradation of wood flour. Experiments were run at 170 and 250°C for a reaction time of one hour. Methanol, ethanol, propanol, ethylene glycol, glycerol, phenol and catachol were tested as solvents using aqueous acids of pH 2.5 and 3 as catalyst. Products were fractionated into toluene, acetone and liquor solubles (liquor = acid and organic solvent used as reaction medium) and an insoluble residue. Under the conditions of our tests, catachol, phenol and ethylene glycol were most effective in solubilizing the wood. Insoluble residues obtained were 2, 9, and 18% by weight of dry wood for the three solvents respectively.

The second liquefaction concept being explored entails the hydrolisis of wood followed by hydrogenation of the hydrolyzed slurry. Acid-catalyzed transfer of hydrogen from solvent molecules is being tested for the hydrogenation step. Cyclohexadiene and  $\alpha$ -phellandrene (5-isopropyl-2-methyl-cyclo hexadiene) were selected as two representative reagents of partially hydrogenated lignin-derived solvents. Tests were run at 250°C for one hour using aqueous acid (of pH 2.5 and 3) as catalyst. The acid pH appeared to have little effect on the yield of toluene and acetone soluble products under these conditions. A carbon balance over the product fractions indicated that substantial amounts of  $\alpha$ -phellandrene was incorporated into the products. When cyclohexadiene was used as the hydrogen donor solvent about 30% of the wood flour was converted to products soluble in acetone.

In the second task, the effects of process variables on the yields and quality of products are being studied for three catalysts: sodium carbonate, ferric chloride and hydrogen iodide. During this quarter we have run experiments using aqueous sodium carbonate solution and ferric chloride solutions as catalysts. The effect of catalyst concentration on the yields of toluene, acetone and water soluble materials was studied for the aqueous sodium carbonate system. In three runs, the reactants (wood flour, 1 part; sodium carbonate solution, 4.4 parts) were heated to 360°C in about one hour and then rapidly cooled. For one run the reactants were held at 360°C for one hour, whereas in another run the time for heating up to 360°C was one hour and 45 minutes. Catalyst concentration of 0, 1, 4, 12, and 20% by weight of the solution were tested. In cases where catalyst was present, toluene solubles ranged from 10 to 15% and water solubles from 17 to 19%. In the absence of the catalyst about 7% of the wood was converted to toluene soluble material and about 4% to water solubles. Between 13 and 21% acetone soluble, toluene insoluble materials were recovered in each case. These results suggest that, over the ranges of our tests, catalyst concentration, heat-up rate,

and time at temperature have little effect on the yield of oil. We have not yet completed product characterization and so do not know if such changes in operating conditions effect the quality of the oil.

The effects of reaction temperature, residence time, catalyst concentration, presence of reducing gases and type of feed (e.g. pre-hydrolyzed slurry vs. wood flour) were determined for the ferric chloride system. Reactions were run at 180°, 250, and 360°C using solutions varying in concentration from 0.8 to 10% ferric chloride by weight. Some runs were done in the absence of carbon monoxide and hydrogen. Residence times of 0.5, 0.75, 1 and 2 hours were tested. Major conclusions are summarized below:

- o Presence of reducing gases (CO/H) is beneficial for liquefaction with ferric chloride.
- o A complex set of reaction occur where toluene soluble materials are further converted to products soluble in either water or acetone.
- o Reaction conditions could be tailored to obtain any of a wide span of products (as indicated by their solubility characteristics)
- o In order to be of possible commercial use the ferric-chloride system must be modified so as to convert the large fraction of insoluble material to more desirable products.

The tasks relating to process improvements and product upgrading are expected to begin in March 1980.

For the task on product characterization our major efforts last quarter were geared towards developing adequate, reproducible product separation procedures for products obtained in the other two tasks. Some spectroscopic work has been completed on selected product fractions. These results will be reported next quarter when more information has been collected.

Subproject B: Catalytic Liquefaction of Biomass

Objective: The objectives of this subproject are:

- o To undertake bench-scale studies leading to improvements in the present liquefaction process.
- o To formulate and conduct exploratory research for the identification and development of new, integrated processes for biomass liquefaction.
- o To investigate the characteristics and stability of biomass liquids.
- o To explore and develop options for the upgrading and utilization of liquids from biomass.

Approach: The selection and development of integrated process concepts generally proceeds in three phases. The first phase involves exploratory catalyst screening. Several potential catalysts are screened at standard conditions based on the chemical approach being pursued. The effect of process variables is then investigated for the most promising catalytic systems. Finally, changes that could result in improved process economics or process operation are tested and evaluated. Two related aspects of the project are concerned with the analysis and characterization of products and with product upgrading and utilization.

The activities of this subproject are related to and co-ordinated with the other two subprojects: Chemical hydrolysis and Engineering development. The liquefaction and hydrolysis subprojects work to interface process steps so as to develop integrated process flow

schemes. Data generated in both the hydrolysis and liquefaction studies will form the basis for engineering process evaluation experiments in a bench-scale process development unit.

Introduction: Work on this subproject began in November 1978. A literature review of the hydrogenation and hydrogenolysis of wood, cellulose, lignin and sugars was first completed. Based on this review, 20 potential catalysts were screened. Both the review and the results of the screening experiments have been reported (1). These experiments led to the identification of ferric chloride as an effective reagent for wood liquefaction.

The subproject contract was renewed in February 1979. Laboratory space was located and refurbished. Major pieces of equipment were purchased and put into operation. The experimental program began again in June 1979. Initial results (presented last quarter) and results obtained this quarter are reported here.

The subproject is divided into five tasks:

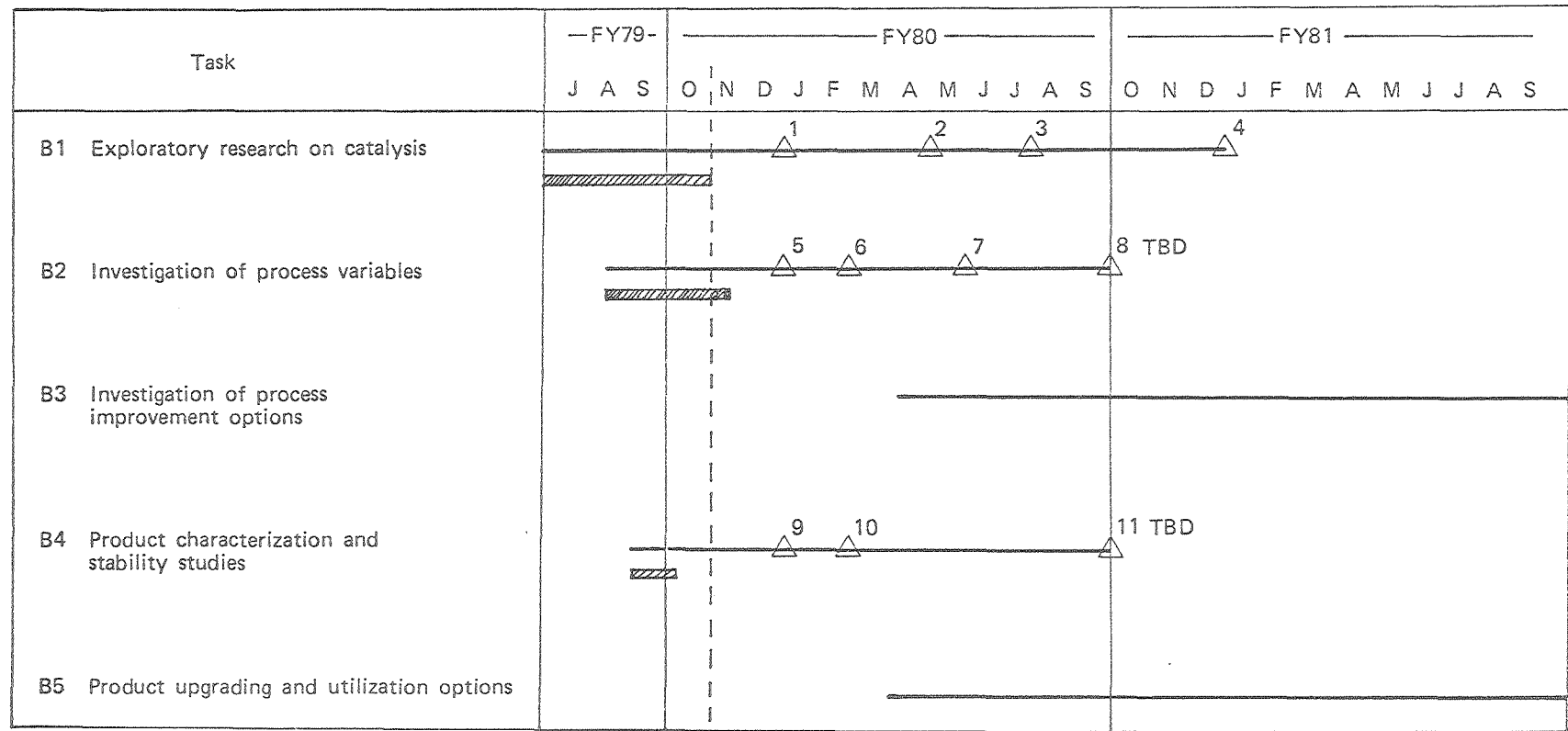
- Task B1: Exploratory Research on Catalysis.
- Task B2: Investigation of Process Variables.
- Task B3: Investigation of Process Improvement Options.
- Task B4: Product Characterization and Stability Studies.
- Task B5: Product Upgrading and Utilization Options.

The subproject schedule chart is shown in Figure 1. As the chart indicates, we expect to work on Tasks B1, B2 and B4 until March 1980. All five tasks will then continue to the end of the fiscal year.

In the task on exploring new catalysts (Task B1), two chemical approaches are being tested for their application to wood



Figure 1. Schedule chart for Subproject B (Catalytic Liquefaction of Biomass).



- 1: Exploration of solvolysis and hydride transfer
- 2: Screening of hydrogenation catalysts
- 3: Exploration of organometallic catalysts
- 4: Screening of homogeneous catalysts
- 5: Process variables for sodium carbonate system
- 6: Process variables for ferric chloride system

- 7: Process variables for HI system
- 8: Process variables for other systems
- 9: Characterizations of sodium carbonate products
- 10: Characterization of ferric chloride product
- 11: Characterization of products from other systems

liquefaction. The first relies on the solvolytic depolymerization of cellulose and/or lignin using acidic mixtures of water and wood-derived organic solvents. Hydrogen transfer from partially hydrogenated lignin-derived solvents is the second approach being tested. In this approach tests are being run to see if hydrogen can be added to wood by the acid catalyzed hydride transfer reaction. We will also test the use of organometallic catalysts and other hydrogenations and decarboxylation catalysts later this year.

The effect of process variables are being studied for three catalytic systems in Task B2. Sodium carbonate catalyzed liquefaction in an aqueous medium (LBL process) is the first catalytic system undergoing tests. The effect of catalyst concentration, reaction time and slurry concentration are being determined at a reaction temperature of  $360^{\circ}\text{C}$ . In the second catalytic system the effects of catalyst concentration, slurrying solvent and reaction time are being tested for the ferric chloride at reaction temperatures of 250 and  $360^{\circ}\text{C}$ . We expect to begin testing the hydrogen iodide system, our third catalytic system, next quarter. The process variables study for the first two systems is also expected to continue next quarter.

In Task B4 products from exploratory experiments and the process variables study are being characterized. Product separation procedures are being developed for each catalytic system. Analysis of selected product fractions will include average molecular weights and nuclear magnetic, ultraviolet and infrared spectrometry. Wet chemical analysis of phenolic, etheric, and hydroxyl groups will also be attempted.

The rationale, procedure and results obtained in each of the three tasks are discussed below.

#### Task B1: Exploratory Research on Catalysis

##### A. Solvolytic Degradation/Hydrogenation System

###### 1. Rationale

Several hydrogenation catalysts have been tested for the production of liquids from wood, cellulose, lignin and sugars (2-4). Raney nickel and copper cromite are probably the best known wood hydrogenation catalysts. Other solid hydrogenation or hydrocracking catalysts could also be effective. In order to hydrogenate wood over a solid catalyst, the wood must first be depolymerized to fine particles or to material soluble in a carrier solvent. The depolymerization and hydrogenation steps could be an integrated if a fraction of the products of wood hydrogenation could be used as the carrier solvent. Solvolysis in an acidic medium could be used for the depolymerization of cellulose (and lignin). If the carrier liquid was also a good solvent for the products of solvolysis a substantial fraction of the wood could be put into solution. A simplified process flow diagram for such a scheme is shown in Figure 2.

To explore the first step in this scheme we have tested the effectiveness of several mixtures composed of aqueous acids and organic liquids known to be produced from the hydrogenation of cellulose and lignin for the solvolysis of wood flour. In coming months we will test the effectiveness of the solvolytic degradation on wood chips and also screen potential hydrogenation catalysts for solvolysis products.

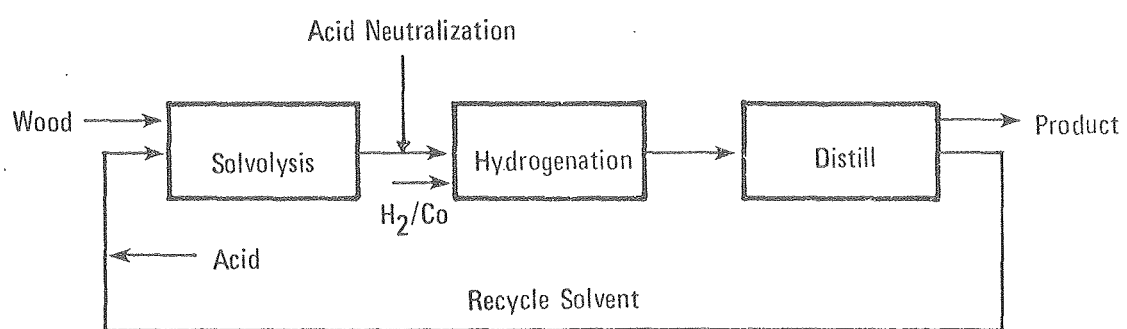


Fig. 2. Simplified flow diagram for solvolysis and hydrogenation of wood.

## 2. Experimental Procedure

All screening experiments were run in a 300 ml Parr reactor. About 15g of wood, 30g of acid and 30g of the organic solvent were weighed into a glass liner. The liner was then placed in the reactor and the reactor sealed. The reactor was flushed several times with hydrogen and charged with 200 psig hydrogen and 200 psig carbon monoxide. The gases were used to keep low boiling solvents as liquids and we do not think they play a role in the reaction. The reactor was then heated to temperature and held there for one hour. At the end of the run the reactor was quickly quenched to room temperature.

Reaction products were passed through a preweighed thimble and the reaction "liquor" (acid and solvent with dissolved products) was collected. The contents of the thimble were then extracted successively with toluene and acetone. Insoluble residue remaining in the thimble was dried in a vacuum oven at  $10^{-2}$  torr and  $110^{\circ}\text{C}$  and weighed. Solvents were evaporated from the acetone and toluene extracts on a rotary vacuum evaporator. The acetone and toluene solubles were then dried under vacuum ( $110^{\circ}\text{C}$ ,  $10^{-2}$  torr) and weighed. Organic solvent and water in the liquor were evaporated and dried in the same way to give a 'liquor soluble' fraction of the product. A schematic representation of the separation procedure is shown in Figure 3.

## 3. Results and Discussion

Both simple and polyhydric alcohols are produced when sugars and/or cellulose are reduced over hydrogenation or hydrogenolysis catalysts.

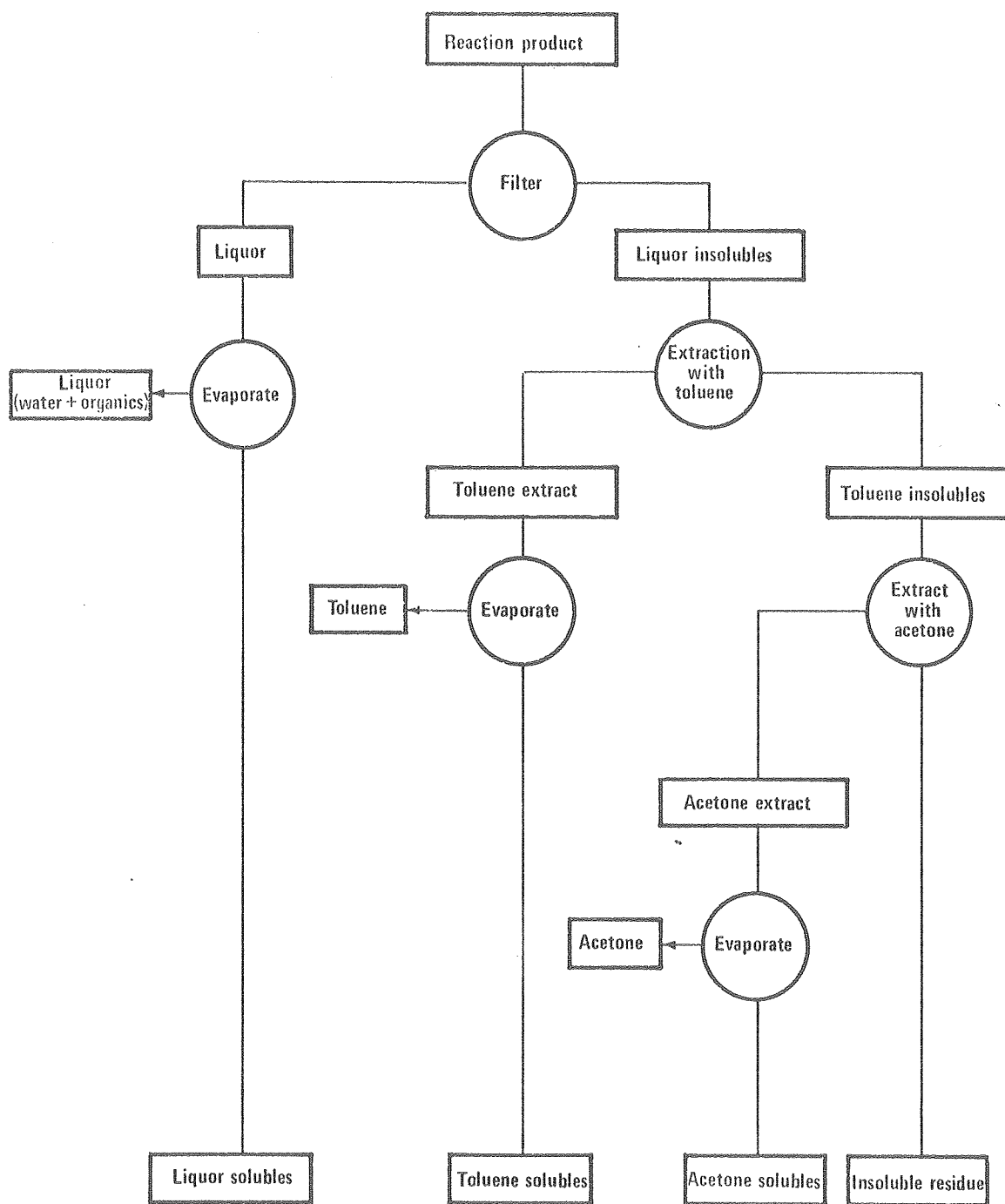


Fig. 3. Product separation procedure for exploratory experiments and low temperature ferric chloride experiments.

Methanol, ethanol, propanol, ethylene glycol and glycerol were screened in order to test the effectiveness of alcohols as recycled solvents for the solvolytic degradation of wood. Catalytic hydrogenation of lignin results in mixtures of phenols, substituted phenols and syringyl and guaiacyl alcohols. Phenol and catachol were selected as representative lower molecular weight lignin--derived solvents for testing. Methanol and ethanol, being the lowest boiling solvents, were tested at 170<sup>0</sup>C. All other solvents were run at 250<sup>0</sup>C. Aqueous sulfuric acid was used as the acid catalyst. Acids of pH 2 and 2.5 were used for runs at 170<sup>0</sup> and 250<sup>0</sup>C, respectively. The presence of water assured a degree of solvolysis (i.e., hydrolysis) for the higher alcohols and phenyl compounds, which may not alkylate the wood as easily as methanol or ethanol. Two experiments were run with acidic water (pH 2.5 and 3) alone for comparison.

Products were separated into fractions soluble in toluene, acetone and reaction liquor (i.e., the acidic-solvent medium), and the remaining insoluble residue. Toluene solubles ranged from about 1% of dry wood for hydrolysis in a pH of 2.5 (Experiment No. RP12), to 22% for propanol (Experiment No. RP21). With most other organic solvents the toluene soluble material ranged between 2 and 10%. Acetone solubles ranged about 5% for solvolysis with propanol to about 36% with catachol. Between 1 and about 60% of the wood was converted to material soluble in the reaction medium at room temperature. Catachol and phenol gave the lowest yields of insoluble material (2% and 9% of

Table 1. Experimental Conditions and Product Yields for Solvolytic Degradation Experiments.

Liquor	Wood flour	1 part	Initial Gases:	
	Acid	2 parts	Hydrogen	200 psig
	Organic Solvent	2 parts	Carbon monoxide	200 psig
	Reaction time	1 hour	Total Pressure	400 psig

$$\Delta P = (\text{Final Pressure} - \text{Initial Pressure}) @ 25^{\circ}\text{C}$$

Mass Recovered = Acetone solubles + Liquor solubles + Toluene solubles + Insoluble Residue.

EXPERIMENT NO.	CONDITIONS			YIELDS (wt - % dry wood)					
	Reaction Temperature	Organic Solvent	PH of Acid	Toulene Solubles	Acetone Solubles	Liquor Solubles	Insolubles Residue	Mass Recovery (wt - %)	$\Delta P$ (Psia)
RP2	250	None*	2.5	1	15	N/D	41	N/D	N/D
RP6	250	None*	3.02	3	13	2	40	58	50
RP8	170	Methanol	2.02	2	29	5	48	84	0
RP7	170	Ethanol	2.02	5	8	1	48	62	20
RP21	250	Propanol	2.5	22	5	13	24	64	45
RP19	250	Ethylene glycol	2.5	4	27	5	18	54	50
RP20	250	Glycerol	2.5	5	135	2	27	169 <sup>+</sup>	65
RP22	250	Phenol	2.5	9	8	61	9	87 <sup>+</sup>	60
RP11	250	Catachol	2.48	N/D	36	N/D	2	N/D <sup>+</sup>	40

\*Wood flour 1 part; acid 4 parts

N/D = not determined

<sup>+</sup> Dried at 200°C and 10<sup>-2</sup> torr



Table 2. Elemental Composition of Products from Solvolytic Degradation Experiments

Wood flour		1 parts	Initial gases									
Acid		2 parts	Hydrogen		200 psig							
Organic Solvent		2 parts	Carbon dioxide		200 psig							
Reaction Time		1 hour	Total pressure		400 psig							

EXPERIMENT NO.	CONDITIONS				ATOMIC RATIOS							
	Reaction Temperature (°C)	Organic Solvent	PH of Acid	Total Mass Recovered wt-%	Toluene Solubles		Acetone Solubles		Liquor Solubles		Insoluble Residue	
					H/C	O/C	H/C	O/C	H/C	O/C	H/C	O/C
RP2	250	None*	2.5	N/D	1.27	0.50	1.2	0.54	1.34	0.71	0.82	0.28
RP6	250	None*	3.02	58	1.18	0.41	1.04	0.33	1.25	0.61	0.83	0.28
RP8	170	Methanol	2.02	84	1.16	0.39	1.26	0.46	1.57	0.70	1.52	0.73
RP7	170	Ethanol	2.02	62	1.10	0.35	1.10	0.34	1.26	0.47	1.48	0.73

\* Wood flour 1 part; acid, 4 parts  
N/D = not determined.

the wood, respectively). Ethylene glycol was the solvent that resulted in the lowest yield of insoluble residue amongst the alcohols (18%).

Phenol, catechol and ethylene glycol are known to be good solvents for lignin. Products obtained in runs using these solvents also had amongst the highest fractions of material soluble in the reaction medium. These results (summarized in Table 1) suggest that lignin solvents form good agents for solvolytic degradation of wood.

In order to determine the extent of gases produced in each run the difference between the initial and final reactor pressure ( $\Delta P$ ) were recorded at 25°C. In general higher gas production (larger  $\Delta P$ ) corresponded to lower amounts of mass recovered in the four product fractions.

Atomic H/C and O/C were determined for all fractions for selected runs. These are shown in Table 2. The Douglas Fir wood flour used had a H/C ratio is 1.3 and O/C ratio of 0.57. In general, the liquor soluble fractions were most hydrated (i.e., highest H/C and O/C ratios).

The distribution of initial carbon in various fractions for some runs is shown in Table 3. Most toluene soluble fractions were tarr-like materials, acetone soluble fractions were generally black solids and insoluble materials were usually fibrous.

Spectrometric analysis and molecular weight determination of selected product fractions are planned next quarter.

Table 3. Carbon Recovery in Products from Solvolytic Degradation Experiments

Wood flour	1 parts	Initial gases	
Acid	2 parts	Hydrogen	200 psig
Organic Solvent	2 parts	Carbon monoxide	200 psig
Reaction Time	1 hour	Total pressure	400 psig

EXPERIMENT NO.	CONDITIONS			CARBON RECOVERED (%)				Total Carbon Recovered (%)
	Reaction Temperature (°C)	Organic Solvent	PH of Acid	Toluene Solubles	Acetone Solubles	Liquor Solubles	Insoluble Residue	
RP2	250	None*	2.5	1	15	N/D	52	68
RP6	250	None*	3.02	4	15	2	52	73
RP8	170	Methanol	2.02	2	32	5	42	81
RP7	170	Ethanol	2.02	5	10	1	43	59

## B. Hydride Transfer

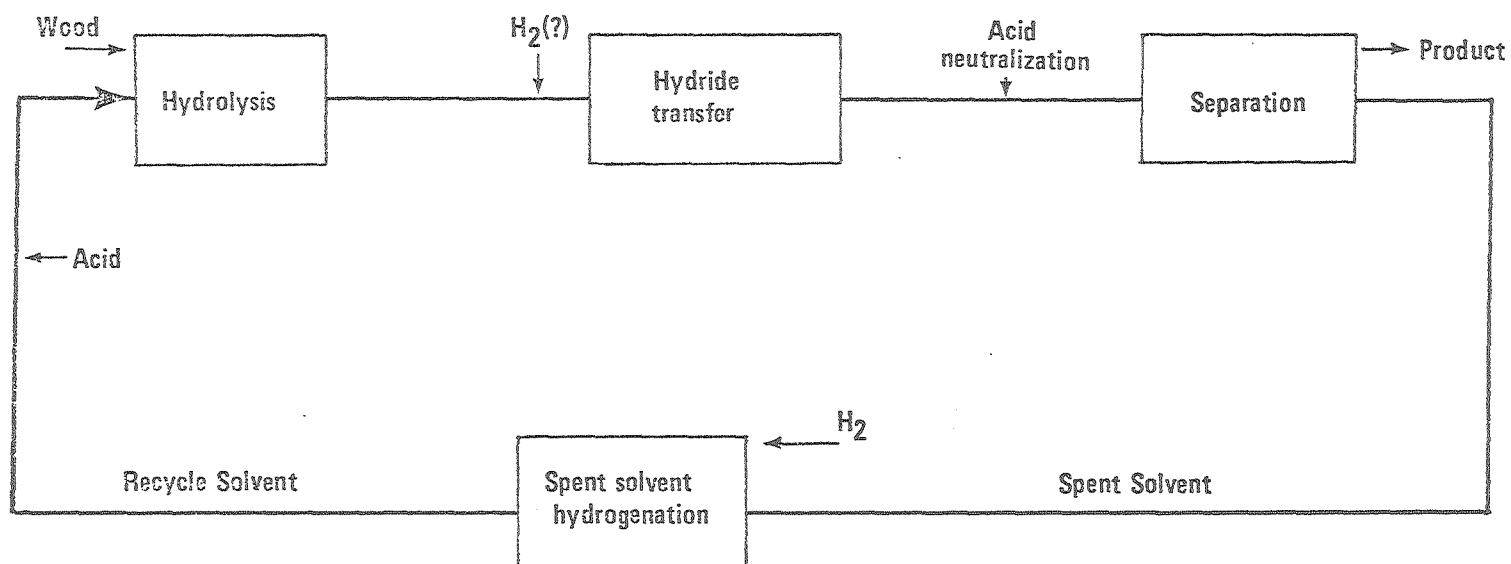
### 1. Rationale

Hydrogenation of solid hydrocarbons such as coal can occur by the donation of hydrogen from organic liquid molecules. Thermal cleavage of bonds followed by hydrogen abstraction from the solvent is the basis of SRC-type coal liquefaction processes. It may be possible to catalytically transfer hydrogen from hydrogen-rich solvents and so effect the reduction of hydrocarbonaceous feeds at lower temperatures. Acid catalyzed hydrogenation (or hydride transfer) may occur from partially hydrogenated organic ring structures. Since some incorporation of solvent could be expected during this reaction, it would be economically beneficial to use partially hydrogenated wood-derived molecules as the hydrogen source for liquefaction. Furthermore, since hydrolysis also occurs in an acidic medium, it may be possible to accomplish both steps using the same carrier solvent. A simplified flow-diagram of such a scheme is shown in Figure 4.

The second step in the process scheme is being tested. Partially hydrogenated forms of products from lignin hydrogenation are being tested as the hydride transfer solvents. In the near future we expect to explore the effect of acid concentration and reaction conditions for hydride transfer from two representative solvents.

### 2. Experimental Procedure

The reaction and product separation procedures used were exactly the same as those for the solvolytic degradation experiment (p. 6-8).



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Fig. 4. Simplified flow diagram for hydride transfer liquefaction of wood.

### 3. Results and Discussion

As a first assumption products of the reduction of lignin by hydride transfer may be considered to be similar to those obtained by lignin hydrogenation. Hydride transfer agents could then be formed by partially hydrogenating phenyl and phenyl propane compounds over appropriate hydrogenation catalysts. Cyclohexadiene and  $\alpha$ -phellandrene (5-isopropyl - 2-methyl - 1, 3 cyclohexadiene) were selected for testing as hydride transfer solvents. Each solvent was tested at 250°C for 1 hour with aqueous sulfuric acid pH of about 2.5 and 3. Yields of toluene, acetone and liquor soluble fractions for all four runs are shown in Table 4.

About 75-80% of the organic wood were solubilized in all four experiments. Acetone soluble yields were between 30 and 35% with cyclohexadiene and 22% with  $\alpha$ -phellandrene. The pH of the acid seemed to make little difference to yield and atomic H/C and O/C of product fractions for both solvents, as shown in Tables 4 and 5. The carbon recovery in each fraction and total carbon recovery, shown in Table 6, indicate extensive alkylation of products when  $\alpha$ -phellandrene was used as the solvent.

To test if any hydrogen transfer occurs from the solvent, spent solvent will be analyzed for benzene and phenylpropane, respectively.

Table 4. Experimental Conditions and Product Yields for Hydride Transfer Experiments.

Liquor	Wood flour	1 part	Initial Gases:	
	Acid	2 parts	Hydrogen	200 psig
	Organic Solvent	2 parts	Carbon monoxide	200 psig
	Reaction time	1 hour	Total Pressure	400 psig

$\Delta P = (\text{Final Pressure} - \text{Initial Pressure}) @ 250^\circ\text{C}$

Mass Recovered = Acetone solubles + toluene solubles + liquor solubles + Insoluble Residue.

EXPERIMENT NO.	CONDITIONS				YIELDS (wt - % dry wood)				
	Reaction Temperature ( $^\circ\text{C}$ )	Organic Solvent	PH of Acid	Toulene Solubles	Acetone Solubles	Liquor Solubles	Insolubles Residue	Mass Recovery (wt - %)	$\Delta P$ (Psia)
RP4	250	Cyclohexadiene	2.52	N/D	30	5	9 <sup>+</sup>	44	50
RP5	250	Cyclohexadiene	2.95	N/D	34	2	26	62	30
RP9	250	$\alpha$ -Phellandrene	2.48	29	22	12	21	84	50
RP10	250	$\alpha$ -Phellandrene	3.03	30	22	19	17	88	20

<sup>+</sup> Probably in error due to material losses.

Table 5. Elemental Composition of Products from Hydride Transfer Experiments.

Wood flour	1 part	Initial gases									
Acid	2 parts	Hydrogen	200 psig								
Organic Solvent	2 parts	Carbon Monoxide	200 psig								
Reaction time:	1 hour	Total Pressure	400 psig								

EXPERIMENT NO.	CONDITIONS			ATOMIC RATIOS							
	Reaction Temperature (°C)	Organic Solvent	pH of Acid	Toulene Solubles		Acetone Solubles		Liquor Solubles		Insoluble Residue	
				H/C	O/C	H/C	O/C	H/C	O/C	H/C	O/C
RP4	250	Cyclohexadiene	2.52		N/D	1.1	0.37	1.25	0.40	0.90	0.25
RP5	250	Cyclohexadiene	2.95		N/D	1.1	0.26	1.29	0.56	0.91	0.24
RP9	250	$\alpha$ -Phellandrene	2.48	1.5	0.04	1.1	0.16	N/D	N/D	0.99	0.22
RP10	250	$\alpha$ -Phellandrene	3.03	1.5	0.05	1.1	0.17	N/D	N/D	1.0	0.23

N/D = not determined



Table 6. Carbon Recovery in Products from Hydride Transfer Experiments.

Wood flour 1 part		Initial gases		
Acid	2 parts	Hydrogen	200 psig	
Organic Solvent	2 parts	Carbon Monoxide	200 psig	
Reaction time:	1 hour	Total Pressure	400 psig	

EXPERIMENT NO.	Conditions				% of Initial Carbon in:			
	Reaction Temp (°C)	Organic Solvent	PH of Acid	Toluene Soluble	Acetone Solubles	Liquor Solubles	Insoluble Residue	Total Carbon Recovery (%)
RP4	250	Cyclohexadiene	2.52	N/D	41	6	12	59
RP5	250	Cyclohexadiene	2.95	N/D	45	2	34	81
RP9	250	$\alpha$ -Phellandrene	2.48	46	31	N/D	28	N/D
RP10	250	$\alpha$ -Phellandrene	3.03	46	31	N/D	23	N/D

N/D = Not determined

Task B2: Investigation of Process VariablesA. Aqueous Sodium Carbonate System1. Rationale:

The Bureau of Mines (BOM) process uses a mixture of aqueous sodium carbonate and recycled oil as the carrier solvent for wood liquefaction, whereas the LBL option relies on the acidic hydrolysis of wood chips followed by sodium carbonate catalyzed liquefaction in an aqueous medium. The BOM process has been studied by its conceivers at Pittsburgh, and more recently at the Battell Pacific Laboratories. The effect of process variables on the aqueous (LBL) system has, however, never been systematically evaluated. We have recently begun to determine the effect of catalyst concentration, slurry concentration and reaction time on the yield and quality of the products obtained during aqueous sodium carbonate catalyzed liquefaction. This study is expected to continue for the next two months and to provide a data base for runs to be made in our process evaluation unit.

2. Experimental Procedure

All sodium carbonate experiments were run in a one liter Autoclave reactor. About 50g of wood flour and 220g of aqueous sodium carbonate solution was used for each run. The autoclave was sealed and flushed several times with hydrogen and then charged with 300 psig of  $H_2$  and 300 psig of  $CO$ . The reactor and its contents were heated to  $360^{\circ}C$  in 40-55 min. and held there for the desired reaction time. At the end of the run the autoclave was cooled and the products removed.

Three different product separation procedures were tested. In the first procedure (see Figure 5) the entire product was passed through dried, preweighed thimbles. The sodium carbonate solution containing dissolved organics--called liquor--was evaporated and dried under vacuum ( $110^{\circ}\text{C}$ ,  $10^{-2}$  torr) to get a liquor soluble fraction. The thimbles were successively extracted with toluene and acetone. The remaining insoluble residue was dried under vacuum and weighed. Acetone was removed from the acetone extract on a rotary evaporator. The acetone extract was vacuum dried to obtain a toluene insoluble, acetone soluble fraction. The toluene extract was freed of solvent by evaporation and then slurried with acetone to obtain an acetone soluble, toluene soluble fraction. The acetone insoluble fraction of the toluene soluble material was a brown powder at room temperature. This powder was further fractionated by extraction with a mixture of toluene and water. Both liquid phases were separated and evaporated. A water and a toluene soluble fraction were thus obtained. Separation in this way showed the presence of a toluene insoluble material that melted below  $110^{\circ}\text{C}$  (the temperature at which toluene extraction occurs) and so passed through the thimble to be recovered as toluene extract. This material was soluble in water.

The product separation procedure was then changed so as to recover acetone, toluene, and water soluble fractions. The second separation procedure is shown schematically in Figure 6. Reaction liquor was first removed by pulling the liquid layer into an erlenmyer flask held

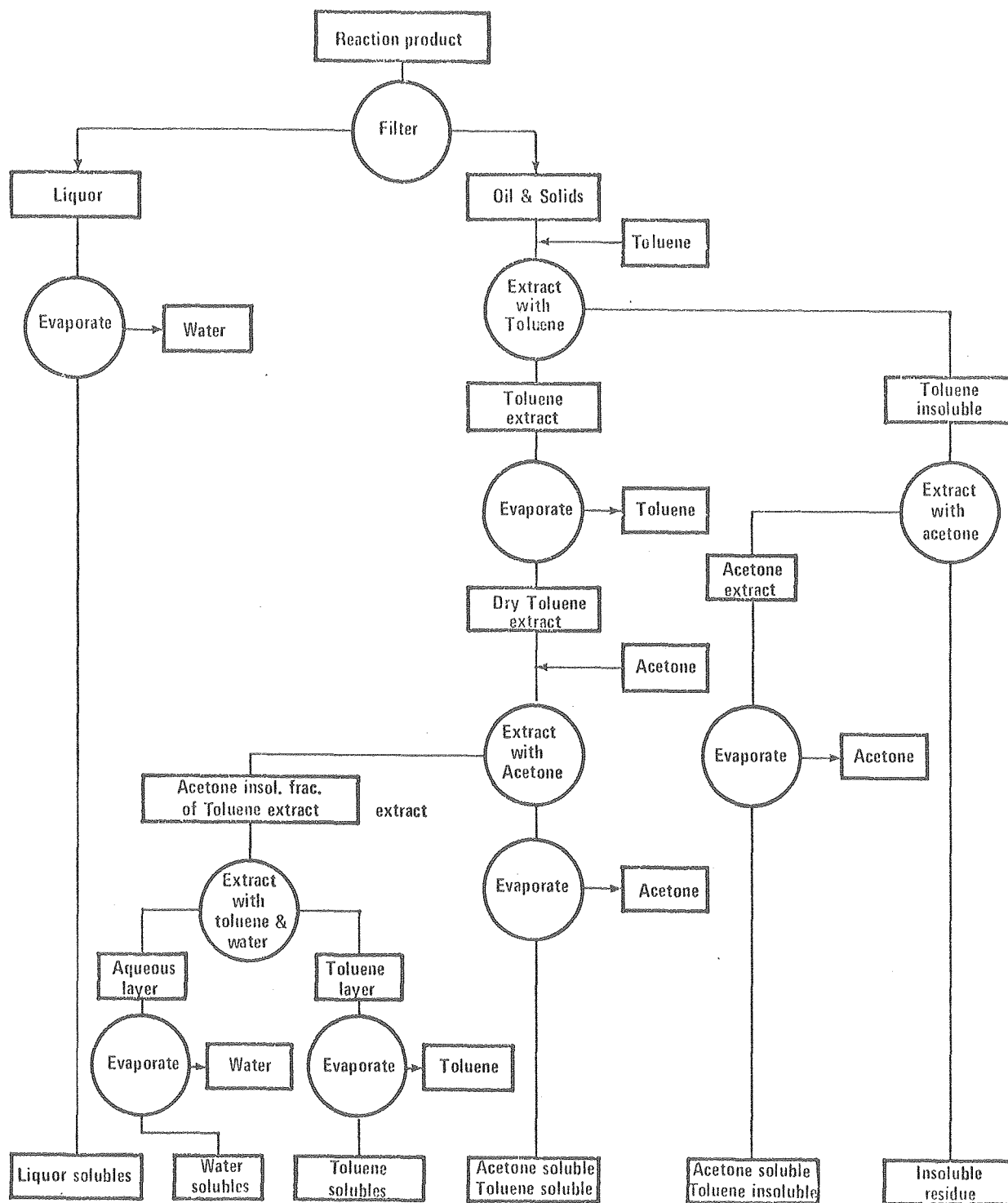


Fig. 5. First separation procedure for products from sodium carbonate catalyzed liquefaction.

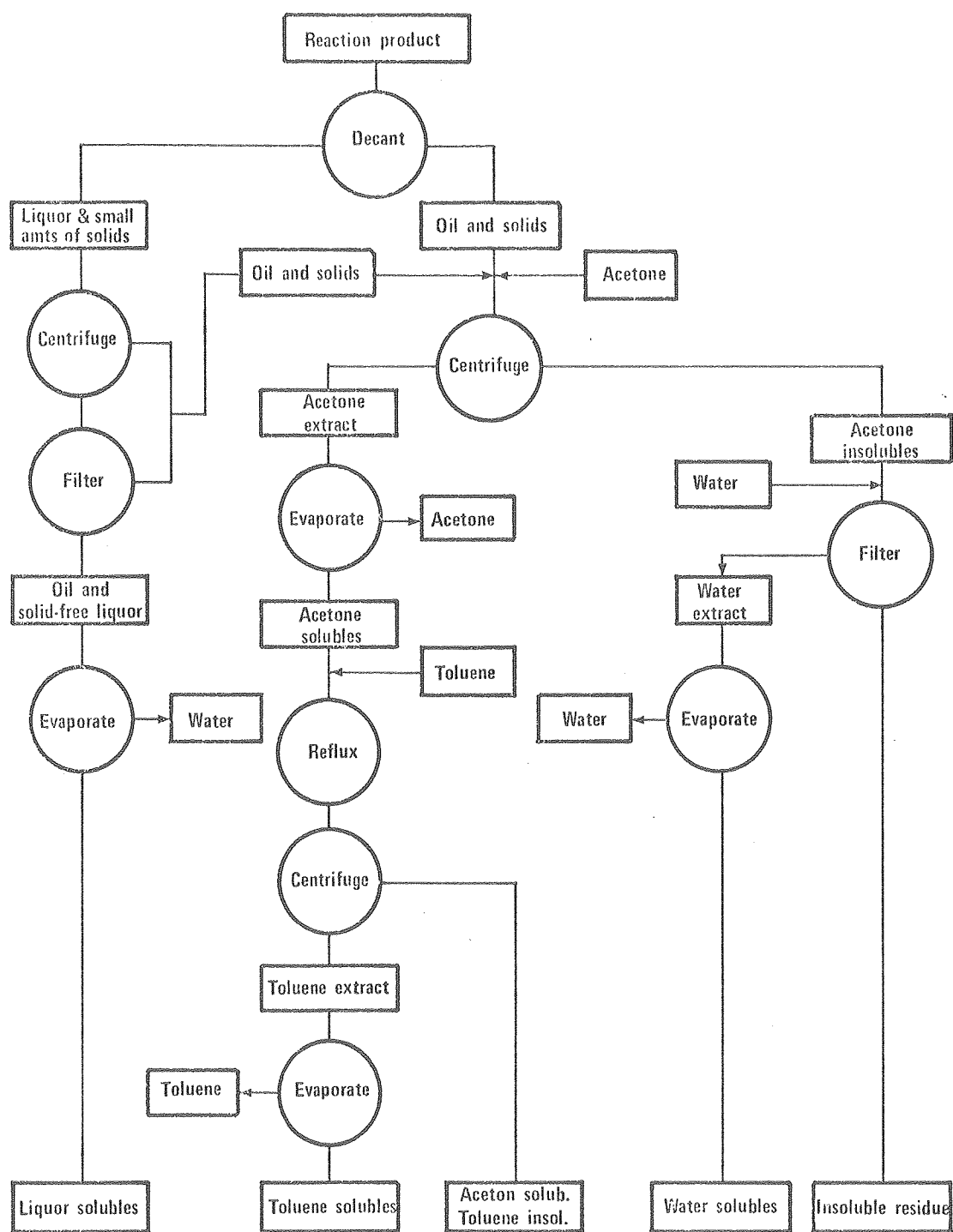


Fig. 6. Second separation procedure for products from sodium carbonate liquefactions.

under vacuum. The liquor contained small amounts of a tarry material, which was removed by centrifugation and filtration and added back to the remaining product in the reactor.

The tarr-like material in the reactor was washed out with acetone. Acetone solubles in the product were recovered by washing several times with 100 ml aliquots of fresh acetone. After each addition of acetone the slurry was centrifuged and the extract decanted.

The acetone insoluble material was mixed with water and filtered through a dry, preweighed sintered glass filter funnel. Insoluble residue was vacuum dried ( $110^{\circ}\text{C}$ ,  $10^{-2}$  torr) and weighed. Acetone from the acetone extract, water from the filtrate and water from the clarified liquor were each evaporated on a rotary vacuum evaporator. Liquor, water and acetone solubles were vacuum dried as usual. The acetone extract was then refluxed with toluene at  $100^{\circ}\text{C}$  for 8 hours and the toluene insoluble material separated by centrifugation. The toluene extract was evaporated and dried to obtain a toluene soluble fraction.

The separation procedure was modified so as to speed up the product separation and reduce the amount of acetone used for extraction. The final separation procedure (to be used in all subsequent runs) is shown in Figure 7. This procedure is similar to the one described above. Instead of cold extraction with acetone and water, both these extractions are done successively in a Soxhlet extractor.

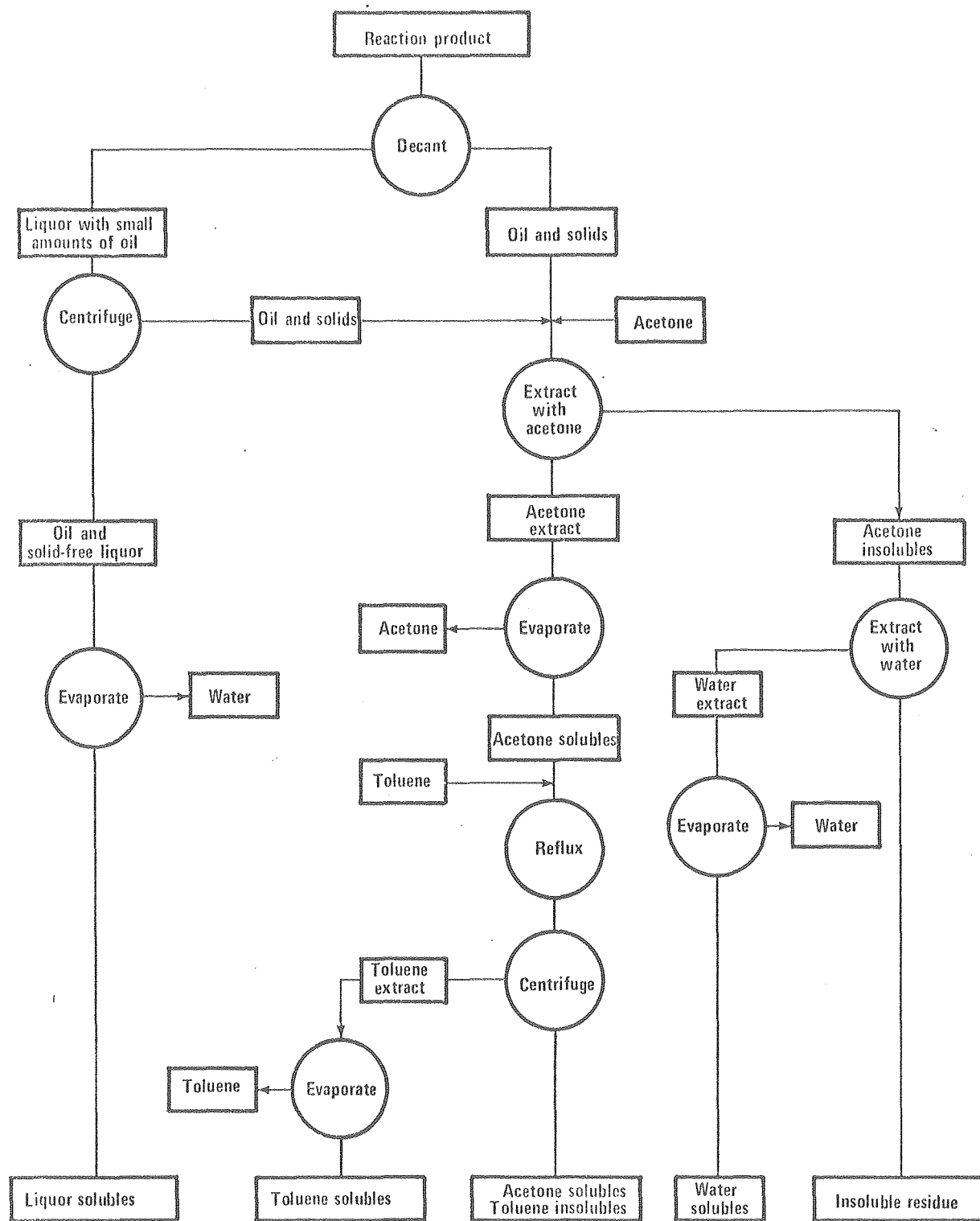


Fig. 7. Final separation procedure for sodium carbonate liquefaction products.

### 3. Results and Discussion

During this quarter we have evaluated the effect of sodium carbonate solution concentration in the aqueous catalytic system. Experiments were run using sodium carbonate concentrations from 20% to 0% by weight of the solution. The reactants were heated to 360°C at various rates. Heat-up time ranged from 40 min to 1 hr, 45 min. In one run (experiment RA3) the reactants were held at 360°C for 1 hr, in all the other runs the reactants were cooled down as soon as they reached 360°C. Relatively mild reaction conditions were selected for these tests so as to better distinguish the effect of solution concentration.

Products were fractionated into toluene acetone, water and liquor soluble materials. Reaction conditions and product yields are shown in Table 7. The amount of sodium present in each fraction was determined by atomic adsorption. Sodium contents of each fraction were then converted to the equivalent sodium carbonate and fraction yields corrected to a sodium-carbonate-free basis. Toluene soluble fractions of products ranged from 10 to 15% by weight of oven dry wood and appeared to be only marginally dependent on the heat-up rate, sodium carbonate concentration and reaction severity (i.e., time at temperature). When no catalyst was used yield of the toluene-soluble fraction dropped to about 7%.

Acetone soluble, toluene insoluble fractions were obtained for three runs (experiments RA7, RA8 and RA9). The acetone solubles ranged from 13 to 15% and under the conditions of our tests, appeared to be



Table 7. Experimental Conditions and Product Yields for Aqueous Sodium Carbonate Liquefaction Experiments.

Wood flour	1 part,	Sodium Carbonate Solution 4.4 parts.												
$\Delta P = (\text{Final Pressure} - \text{Initial Pressure}) @ 25^{\circ}\text{C}$														
Mass Recovered = Toluene solubles + Acetone Solubles + Water Solubles + Liquor Solubles + Insoluble Residue														
EXPERIMENT NO.	CONDITIONS						YIELDS (wt % dry wood)*							
	Final Temp. (°C)	Heat-Up Time (min)	Time at Temp (min)	Gases	Cold Pressure (psig)	Sodium Carbonate Soln. Conc. (wt %)	Toluene Solubles	Acetone Solubles	Water Solubles	Liquor Solubles	Insoluble Residue	Mass Recovered (wt-%)	P (Psia)	Product Separation Procedure
RA3	360	55	60	CO/H <sub>2</sub>	400/400	20	15	4	9	10	7	45	N/D <sup>+</sup>	1
RA7	360	48	0	CO/H <sub>2</sub>	350/300	12	12	13	1	16	2	44	250	2
RA8	360	42	0	CO/H <sub>2</sub>	300/300	4	10	15	18		4	47	210	3
2	340	105	0	CO/H <sub>2</sub>		1.02	14	21			8	42	N/D	3
RA9	360	39	0	CO/H <sub>2</sub>	300/300	0	7	13	--	4	25	49	90	3

27

N/D = not determined

\* Reported on a sodium carbonate free basis.

<sup>+</sup> Gases vented 3 times at 360°C to keep reaction pressure at 4,500 psig.

independent of the catalyst concentration, the same yields were obtained without any catalyst.

Total water solubles (i.e., material soluble in the reaction liquor + material obtained by water extraction) were determined for experiments RA3, RA7 and RA8. In each case between 17 and 19% of the starting wood appeared as water-solubles. In the absence of sodium carbonate only 4% of the products dissolved in water.

Insoluble residue ranged from 2 to 8% of the wood and generally increased with decreasing sodium carbonate concentration. When no sodium carbonate was present about 25% of the wood was obtained as an insoluble residue.

The yields of soluble fractions and insoluble residue from experiment RA3 may be incorrect because gases were vented at reaction temperature to prevent exceeding the safe operating pressure of the reactor. Low-boiling materials may have been lost and condensation reactions encouraged due to gas venting.

Between 42 and 47% of the original wood was accounted for in each run where catalyst was present, and about 50% of the original wood was recovered in the absence of a catalyst.

To characterize product fractions, Ultimate analysis was done for each fraction of products obtained in experiment RA7. Table 8 shows the atomic H/C and O/C ratios and carbon recovered in each product fraction for experiment RA7. Amongst the soluble fractions the toluene solubles contained the least amount of oxygen per carbon atom (O/C = 0.11). Atomic O/C ratios of the acetone solubles were

Experiment RA7: Reaction Conditions

Toluene Solubles	Acetone Solubles	Water Solubles	Liquor Solubles	Insoluble Residue
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## Atomic Ratios\*

% Initial Carbon in Fraction\*

Total  
Carbon  
(%)

18.0	19.4	1.2	25.7	2.5	66.8
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\* On a  $\text{Na}_2\text{CO}_3$  - free basis

comparable to those of the toluene soluble material. The toluene soluble fraction had an atomic H/C of 1.25 which was significantly higher than that of the acetone soluble fraction ( $H/C = 0.18$ ). Fractions soluble in water had similar O/C ratios (about 0.66), whereas product soluble in the reaction liquor had a considerably higher H/C ratio than product obtained by extraction with water.

About 67% of the initial carbon was recovered in the various product fractions.

Average molecular weights and spectroscopic analysis of different product fractions is underway. More conclusive comments on the nature of the products may be possible when additional information becomes available.

## B. Ferric Chloride System

### 1. Rationale:

In the LBL modification of the BOM process, wood chips are hydrolyzed with dilute acid to form a pumpable slurry which is then liquefied using a basic catalyst (sodium carbonate). Another option would be to use an acidic catalyst effective both for hydrolysis and liquefaction. Initial screening experiments (1) indicated that ferric chloride may be a good reagent for liquefaction. Dilute solutions of ferric chloride were also found to hydrolyze wood chips. The ferric chloride system is being further evaluated by testing for the effect of process variables on the yield and quality of the products.

## 2. Experimental Procedure

Experiments with ferric chloride were done at 180°C, 250°C and 360°C. A 300 ml Parr reactor vessel with an internal glass liner was used for reactions run at 180 and 250°C. Product separation procedures for these experiments were identical to those used for exploratory experiments (see Figure 3). Reaction products were poured through a preweighed thimble, and the liquor so obtained was evaporated to give liquor solubles contents of the thimble were successively extracted with toluene and acetone in a Soxhlet apparatus. Toluene and acetone were removed from the extracts on a rotary vacuum evaporator. The toluene soluble, acetone soluble and insoluble fractions were dried in a vacuum oven at 100°C and  $10^{-2}$  torr.

Reactions at 360°C were run in a one liter Autoclave reactor. About 30g of wood flour and 120g of ferric chloride solution were placed in the reactor. The reactor was then sealed, pressure tested, flushed several times and then charged with gas.

Reaction were run with gaseous mixtures of carbon monoxide and hydrogen (300 psig each). For some runs the reactor was flushed with nitrogen and then charged with 10 psig nitrogen.

A modified product separation procedure was used for the high temperature ferric chloride experiments. Products were filtered through thimbles as usual. Contents of the thimbles were extracted successively with water and acetone (instead of acetone and toluene). Toluene solubles were obtained by refluxing dry acetone soluble

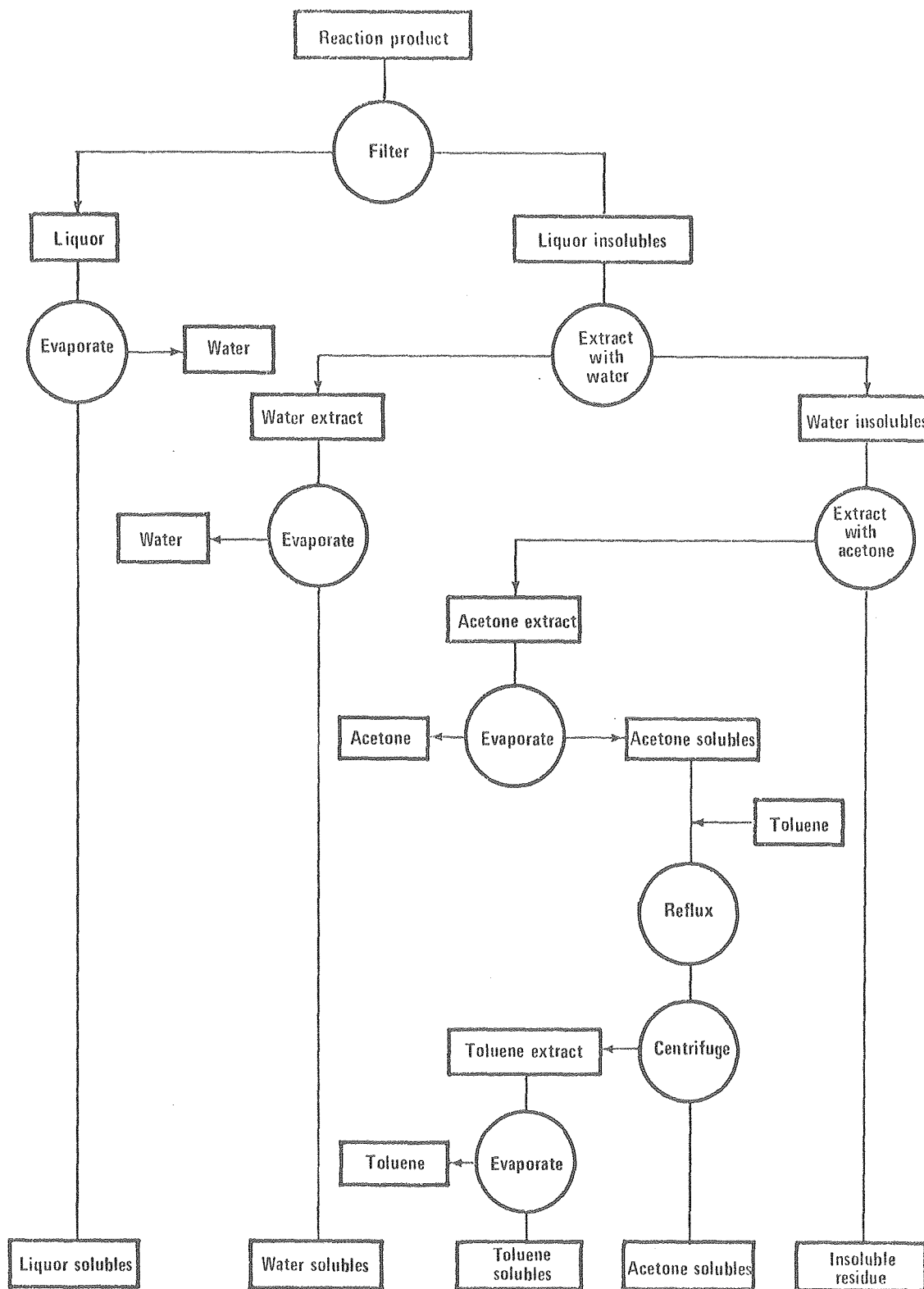


Fig. 8. Product separation procedure for high temperature ferric chloride experiments.

material with toluene and centrifuging the resulting slurry to obtain the toluene extract. The water, acetone and toluene extracts and the insoluble residue were each dried at  $110^{\circ}\text{C}$  and  $10^{-2}$  torr. The separation procedure is shown in Figure 9.

Some runs were made with hydrolyzed slurry instead of wood flour. Hydrolysis of wood chips (or flour) was done in a one gallon autoclave reactor. Reaction conditions of hydrolysis with ferric chloride solutions are shown in Table 9. Products from hydrolysis Runs 1 and 2 were used for subsequent liquefaction without any change. Hydrolyzed slurry from Run HP-17 was refined prior to liquefaction. All experimental results of wood treated with ferric chloride are discussed below.

### 3. Results and Discussion

The effectiveness of ferric chloride as a reagent for liquefaction was tested at temperatures of  $180^{\circ}$ ,  $250^{\circ}$  and  $360^{\circ}\text{C}$ . The fraction of product soluble in toluene, acetone and reaction liquor and the insoluble residue were determined for each run at  $180^{\circ}$  and  $250^{\circ}\text{C}$ . The effect of ferric chloride concentration, reaction time and reducing gases on the yield of product fractions were determined both for wood flour and pre-hydrolyzed slurries. Reaction conditions and product yields are shown in Table 10.

The insoluble residue obtained usually varied between about 28 and 45% of the starting wood. Within this range an increase in ferric chloride concentration led to a small reduction in insoluble solids

Table 9. Reaction Conditions for Wood hydrolysis with Ferric Chloride Solution.

Experiment No.	Reaction Temp. (°C)	Time to Temperature (min)	Time at Temperature	FeCl <sub>3</sub> Solu. Concentration wt %	Wood/ Solution Ratio	Feed	Product Designation
1	180	10-15	45	0.8	1/4	C	H1
2	180	10-15	45	1.2	1/4	S	H2
HP-17	180	35-45	45	5	1/4	C	H3

C = wood chips; S = wood flour

These experiments were done by Larry Schaleger and Nasser Yaghoubzadeh.



at 180°C. Ferric chloride concentrations higher than 1.2% appeared to have little effect on the yield of insoluble solid at 250°C for reaction times of 1 hr or more.

Where no reducing gases were used the toluene soluble fractions of the product appeared to depend on reaction time and ferric chloride solution concentration at 180 and 250°C. At the lower temperature an increase in residence time from 1 to 2 hrs resulted in a decline in toluene solubility from about 14% to 0.4%. (Compare experiments RP13 and 15). An increase in ferric chloride concentration from 5 to 10% at 250°C resulted in a decrease in toluene solubility from 13 to 1% by weight of oven dry wood. These results suggest that at a given reaction temperature and ferric chloride concentration there exists an optimum residence time where maximum yield of toluene soluble material is obtained. Such maxima usually occur in consecutive reactions, where the product of one reaction is further connected by a second (consecutive) reaction.

Comparison of experiments 8, 11 and 10 shows that under a reducing atmosphere, at 250°C, the acetone soluble fraction of the product increases with ferric chloride concentrations for catalyst concentrations of up to 5% and then remains essentially unchanged. At low ferric chloride concentrations (e.g., 0.8%; experiment 7) low acetone solubles are obtained even if the reaction time is increased.

Wood flour and hydrolyzed slurry are both converted at about the same rate as indicated by the insoluble fractions obtained in experiments RP1 and 9.

Table 10. Experimental Conditions and Product Yields for Low Temperature Ferric Chloride Experiments.

Wood: 1 part

Ferric Chloride Solution: 4 parts

 $\Delta P = (\text{Final Pressure} - \text{Initial Pressure}) @ 25^\circ\text{C}$ 

Mass Recovered = Toluene Solubles + Acetone Solubles + Liquor Solubles + Insoluble Residue

Experiment No.	Reaction Conditions						Yields (wt-% dry wood)					
	Reaction Temp $^\circ\text{C}$	Reaction Time (hr)	Type of Feed	FeCl <sub>3</sub> Solu. Conc. %-wt.	Gases	Cold Pressure psig	Toluene Solubles	Acetone Solubles	Liquor Solubles	Insoluble Residue	P (psia)	Product Separation Procedure
HP-14	180	0.75	C	5	Air	0	5	16	11	55	N/D	
RP14	180	2	S	5	N <sub>2</sub>	15	0	24	3	43	15	1
RP13	180	2	S	10	N <sub>2</sub>	15	14	8	13	40	10	1
RP15	180	2	S	10	N <sub>2</sub>	15	0.4	17	26	39	40	1
7	250	2	H1	0.8	CO/H <sub>2</sub>	200/200	--	1	N/D	42	N/D	2
8	250	1	H2	1.2	CO/H <sub>2</sub>	200/200	--	8	N/D	31	N/D	2
11	250	1	S	5	CO/H <sub>2</sub>	200/250	--	23	N/D	33	N/D	2
RP1	250	1	S	5	N <sub>2</sub>	10	13	1	14	28	120	1
9	250	1	H1	5	CO/H <sub>2</sub>	200/200	--	20	N/D	32	N/D	2
10	250	2	H2	5	CO/H <sub>2</sub>	200/200	--	24	N/D	31	N/D	2
RP12	250	1	S	10	N <sub>2</sub>	15	1	13	23	39	125	1
RP16 <sup>+</sup>	250	1	S	5	N <sub>2</sub>	15	16	2	4	36	60	1
RP17 <sup>*</sup>	250	1	S	5	N <sub>2</sub>	15	0.2	4	24	28	15	2

\* Wood flour, 1 part; FeCl<sub>3</sub> Solution 2 parts; Ethanol 2 parts

N/D - not determined. C = wood chips, S = flour, H1, H2 = hydrolyzed slurry (see Table 9).

<sup>+</sup> Compare with RP-1

Runs made at 360°C are shown in Table 11. Wood flour and ferric chloride solution (or hydrolyzed slurry) were heated to 360°C in about 1 hr. The effect of hydrolysis, and reducing gases were tested under these conditions. In the absence of reducing gases (experiments RA1 and 2) the insoluble residue was comparable when either pre-hydrolyzed slurry or wood flour was used as feed, at ferric chloride solution concentration of 0.8%. About 60% of the starting wood was accounted for in the identified products with the rest probably forming gases as indicated by a substantial increase in gas pressure. In the presence of reducing gases, about 97% of the starting wood was accounted for, with the roughly the same amount of gas production. Since any water formed is lost in our separation procedure, a possible explanation of the lower mass recoveries may be that in the absence of reducing gases considerable dehydration of wood occurs with increased water formation. This possibility will be verified when Ultimate analysis of products are obtained.

Higher fractions of toluene and water soluble products were obtained in the presence of reducing gases, which also suggests a greater amount of oxygen and hydrogen in the product in comparison to runs done without reducing gases.

To determine the effect of more severe reaction conditions on product yield two experiments were run in which the reactants were heated to 360°C in about 1 hr and held at temperature for 30 min (experiments 5 and RA6). Yields of insoluble residue were about 24

Table 11. Experimental Conditions and Product Yields for High Temperature Ferric Chloride Experiments.

Wood, 1 part

Ferric Chloride Solution: 4 parts

$\Delta P = (\text{Final Pressure} - \text{Initial Pressure}) @ 250^\circ\text{C}$

Mass Recovered = Toluene Solubles + Acetone Solubles + Water Solubles + Insoluble Residue

Experiment No.	Reaction Conditions						Yields (wt-% dry wood)							
	Final Reaction Temp. ( $^\circ\text{C}$ )	Heat-Up Time (min)	Time at Temp (min)	FeCl <sub>3</sub> Solu. Conc. wt.-%	Feed	Gases	Cold Pressure Temp.	Toulene Solubles wt.-%	Acetone Solubles wt.-%	Water Solubles wt.-%	Insoluble Residue wt.-%	Total Mass Recovered wt.-%	$\Delta P$ (psia)	Product Work-Up Procedure
RA2	360	64	0	0.8	S	N <sub>2</sub>	10	0.6	8.6	12.0	36.8	58.0	70	2
2R	360	60	0	0.8	H1	CO/H <sub>2</sub>	800	N/D	23.0	24.0	50.4	97.4	110	2
RA1	360	65	0	0.8	H1	N <sub>2</sub>	10	2.8	9.6	9.0	40.4	61.8	100	2
5	365	60	30	1.2	H2	CO/H <sub>2</sub>	600	N/D	8.4	67.4	24.1	99.9	100	2
RA6	360	57	30	5	H3	N <sub>2</sub>	10	3.8	6.5	8.0	31.5	50.2	270	2

S = wood flour

H1, H2, H3 = hydrolyzed slurry (see Table 9)

and 32% for ferric chloride concentrations of 1.2 and 5 wt%, respectively. Excessive gasification occurred under these conditions in the absence of reducing gases, as indicated by the mass recovered and change in gas pressure. The net yield of acetone soluble material was comparable for both runs (about 9%), but water soluble fraction of product was about 6 times greater when reducing gases were used.

These results suggest that

- o Presence of reducing gases (CO/H) is beneficial for liquefaction with ferric chloride.
- o A complex set of reaction occur where toluene soluble materials are further converted to products soluble in either water or acetone.
- o Reaction conditions could be tailored to obtain any of a wide span of products (as indicated by their solubility characteristics)
- o In order to be of possible commercial use the ferric-chloride system must be modified so as to convert the large fraction of insoluble material to more desirable products.

We plan to continue studying the ferric chloride system in the coming months. The feasibility of using co-catalysts that enhance the yield of liquids and the use of non-aqueous slurries will be explored.

Task B4: Product Characterization and Stability Studies

Over the last quarter the major effort in this task was geared toward developing adequate separation procedures. Methods for separation of products for each catalytic system have been discussed in the appropriate sections.

We have also begun spectrometric analysis and molecular weight determinations of selected product fractions. These results will be presented in the next quarterly report by which time we hope to collect more conclusive information on possible chemical structures in product fractions.

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